

CATALYTIC HYDRODENITROGENATION OF AN SRC-II COAL LIQUID.  
EFFECT OF HYDROGEN SULFIDE

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The first step in coal liquefaction yields coal liquids which are high in nitrogen, sulfur, and oxygen. These heteroatoms must be removed before these coal liquids can be transformed into synfuels or petrochemical substitutes. However, the catalytic removal of nitrogen (HDN) and oxygen (HDO) consumes excessive amounts of hydrogen. This excess hydrogen is consumed in the hydrogenation of aromatics. If it were possible to remove the nitrogen and oxygen from coal liquids with a minimum of hydrogen and at lower temperatures than currently used, coal could become an economically viable energy source.

Workers have shown that HDN catalysis of model systems undergoes significant rate enhancement in the presence of  $H_2S$  (1-5), and some enhancement in the presence of  $H_2O$  (6,7). Other workers (8,9) have shown that the acidity of the support is important in the enhancement of HDN activity.

We have recently suggested, based on mechanistic studies of HDN of nitrogen heterocycles that nucleophiles such as  $H_2S$ ,  $H_2O$ , and perhaps  $NH_3$  can enhance catalysis by promoting heterocyclic ring opening via nucleophilic attack on the metal-complexed heterocycle (10). We have also seen in our work that the addition of acids aids in the hydrogenation of nitrogen containing heterocycles (11). Thus it may be possible to increase the rate of hydrogenation of heterocycles while not effecting the rate of hydrogenation of other aromatics.

The objective of this work is to develop an understanding of how nucleophiles such as  $H_2S$ ,  $SH^-$ , and  $S^{2-}$ ,  $H_2O$ ,  $NH_3$ , and added acids effect the HDN process of coal liquids under catalysis conditions. From the results of our work we have found that the addition of  $H_2S$  or added acids to an SRC-II coal liquid enhances the removal of nitrogen under standard HDN conditions.

#### Experimental Procedures and Materials

SRC-II middle distillate was obtained from the Pittsburg and Midway Mining Co. SRC pilot plant at Fort Lewis, Washington. The cobalt-molybdenum catalyst, HT-400 (3 wt% CoO, 15.1 wt%  $MoO_3$ , on  $Al_2O_3$ ) was obtained from Harshaw Chemical Company. Hydrogen sulfide ( $H_2S$ ) was obtained from Matheson. Hydrogen ( $H_2$ ), nitrogen ( $N_2$ ), and an  $H_2S(10\%)/H_2$  gas mixture were obtained from Liquid Carbonic.

#### Apparatus

Hydrogenation reactions were performed in a 300-mL Autoclave Engineers (AE) Magne drive stirred reactor, heated with a 1000-W electric furnace (AE). The temperature was controlled with a model CP temperature controller (AE). The autoclave was connected through a sample gas vent to a Carle Series S gas chromatograph (GC) adapted by Carle to analyze  $C_1-C_3$ ,  $H_2$ ,  $O_2$ ,  $N_2$ , and  $H_2S$ .

#### Analytical Procedures

Nuclear magnetic resonance (NMR) spectra were obtained on a JEOL FX 90Q spectrometer. NMR samples were prepared by mixing one part by weight of coal liquid with two parts of  $CDCl_3$ . The conditions for obtaining the  $^{13}C$  NMR spectra were as follows. Samples were made 0.025 M in  $Cr(AcAc)_3$ . The pulse width was 6  $\mu s$  and pulse delay

15 s. The NNE option (heterodecoupling with no Nuclear Overhauser enhancement) was chosen for quantitative  $^{13}\text{C}$  analyses.

The infrared (IR) spectra were obtained on a Perkin-Elmer 281 spectrophotometer. Elemental analyses were obtained from Galbraith Laboratories. (Nitrogen was determined by the Kjeldahl method).

#### Catalyst Preparation

The HT-400 cobalt-molybdenum catalyst was ground and sieved to obtain a 60- to 200- mesh powder. The catalyst was activated at  $400^\circ\text{C}$  in a flowing mixture of  $\text{H}_2\text{S}$  (10%) in  $\text{H}_2$  for 24 h, then stored in a Vacuum Atmospheres Dri-box under  $\text{N}_2$ . (Before the catalyst was sulfided, it was heated for 2 h at  $400^\circ\text{C}$  under flowing synthetic air, pretreated with  $\text{H}_2\text{S}/\text{H}_2$  mixture for 1 h at room temperature, then slowly heated to  $400^\circ\text{C}$  over a 2-h period). Anal.: Mo, 7.8%; S, 7.75%.

#### Standard Reaction Procedures

The autoclave was filled under  $\text{N}_2$  with the desired quantity of activated catalyst and SRC-II liquid. The reactor was then charged with 1200 psi of  $\text{H}_2$  (or  $\text{H}_2/\text{H}_2\text{S}$ ). For those reactions using  $\text{H}_2\text{S}$  only or when  $\text{NH}_3$  was added, the following procedure was used: A tared 20-mL minireactor was filled with  $\text{H}_2\text{S}$  or  $\text{NH}_3$  to the desired weight. The minireactor was then connected to the 300-mL autoclave and the system was purged with  $\text{N}_2$ . The 300-mL reactor was cooled with dry ice, and the gas was condensed into the autoclave.

The system was heated to  $400^\circ\text{C}$  and maintained at  $400^\circ\text{C}$  for 1 h, at which time the heating furnace was removed. When the reactor had cooled to room temperature, GC analyses were performed on the product gases. The liquid products were removed and filtered to remove the catalyst. Duplicate runs were made at either end of the concentration range (analyzed nitrogen content deviates no more than 0.02% in the duplicate runs).

#### Results and Discussion

##### Treatment of SRC-II with Hydrogen Sulfide (without catalyst)

The data from the reactions of  $\text{H}_2\text{S}$  or  $\text{H}_2\text{S}/\text{H}_2$  with the SRC-II liquid are shown in Table 1. When the SRC-II was treated with  $\text{H}_2\text{S}$  alone, we observed some evolution of gases (1.96 mmol gas/g coal liquid) due to  $\text{H}_2$ , ethane, and propane. The evolution of gases affects the quality of the remaining coal liquids. As determined by NMR, the fraction of aliphatic hydrogen and carbon decreased from 0.66 to 0.60 and 0.32 to 0.30, respectively, and the H/C ratio decreased from 1.20 to 1.15 from the original SRC-II liquid. In contrast, the treatment of the coal liquid with the  $\text{H}_2\text{S}/\text{H}_2$  mixture resulted in essentially no change in hydrogen content from the original. The IR spectra of these reaction products are similar to that of the original liquid and show no absorptions in the region of 2550 to  $2600\text{ cm}^{-1}$  where we expected to see SH stretches. Elemental analyses of the products from the  $\text{H}_2\text{S}$  and  $\text{H}_2\text{S}/\text{H}_2$  reactions showed an increase in sulfur content from 0.30% to 0.54 and 0.43% respectively. These results are in accord with what might be expected based on Stenberg's work at higher temperatures (12) ( $450^\circ\text{C}$  vs  $400^\circ\text{C}$  used here).

##### Treatment of SRC-II with Sulfided Catalyst

In experiments 3 through 9 we treated 50 g of the coal liquid using a 1% concentration of sulfided catalyst. As seen from Table 1 the addition of nucleophiles such as  $\text{H}_2\text{S}$ ,  $\text{HS}^-$ ,  $\text{S}^{=}$ ,  $\text{H}_2\text{O}$ , or  $\text{NH}_3$ , or added acids such as trifluoroacetic acid (TFA), do not have a dramatic effect of the hydrogen uptake (by H/C ratio) or on the aliphatic to aromatic ratios (by NMR) nor were there significant difference in the IR spectra of the products from the runs. However, as seen from the elemental analyses of these

products, the nitrogen content of 0.74% (exp 3) in the baseline run with  $H_2$  decreased to 0.56% (exp 4) in the  $H_2S/H_2$  run, and decreased to 0.42% (exp 9) in the TFA/ $H_2$  run. Figure 1 shows that as the  $H_2S$  or TFA concentration increases, the nitrogen concentration of the resultant hydrotreated product decreases. The addition of  $S^{2-}$  as  $Na_2S$  (exp 7) or the addition of  $H_2O$  (exp 5) to the standard reaction resulted in no enhancement over that of exp 3. The addition of  $NH_3$  seemed to inhibit the HDN reaction (exp 6), whereas the combination of  $NH_3$  and  $H_2S$  resulted in only a slight inhibition of the HDN reaction (exp 8).

Table 1. Reactions with 1% Sulfided Catalyst at 400°C for 1 h with 1200 psig of  $H_2$  (or  $H_2S/H_2$ )

Experiment <sup>a</sup>	Additive (mole wt%) <sup>b</sup>	%N	%S	H/C	%H <sub>alip</sub>	%C <sub>alip</sub>
SRC-II	--	0.98	0.30	1.20	66	32
1c,d	$H_2S$ (0.27)	1.00	0.54	1.16	60	30
2 <sup>d</sup>	$H_2S$ (0.084)	0.92	0.43	1.21	67	33
3	--	0.74	0.04	1.23	71	38
4	$H_2S$ (0.084)	0.56	0.12	1.23	72	40
5	$H_2O$ (0.14)	0.75	--	1.27	72	38
6	$NH_3$ (0.084)	0.99	0.03	1.24	72	37
7	$Na_2S$ (0.084)	0.72	0.18	1.20	73	38
8	$NH_4HS$ (0.084)	0.87	0.15	1.23	73	39
9	TFA (0.054)	0.42	0.15	1.22	70	37

<sup>a</sup>Duplicate runs.

<sup>b</sup>Moles of additive per 50 g of coal liquid.

<sup>c</sup>No hydrogen used.

<sup>d</sup>No catalyst used.

## Conclusions

The addition of free  $H_2S$  under coal liquid upgrading conditions aids in the HDN process. These results validate the HDN modeling studies of Bhide et al. (1) and those of Satterfield (2-5) and are in accord with our predictions (10). Furthermore, in contrast to the runs without catalyst, the addition of  $H_2S$  with catalyst leads to the product that has a reduced sulfur content. Our results also show that TFA aids in the HDN process. Although the HDN enhancement resulting from the addition of TFA is most likely due to its acidic properties, since it decomposes during the HDN reaction it is difficult to determine at what step in the HDN process the acceleration occurs. However our preliminary results are encouraging and with further experimentation we may be able to make substantial improvement in the HDN process which will result in considerable cost benefit.

## Acknowledgement

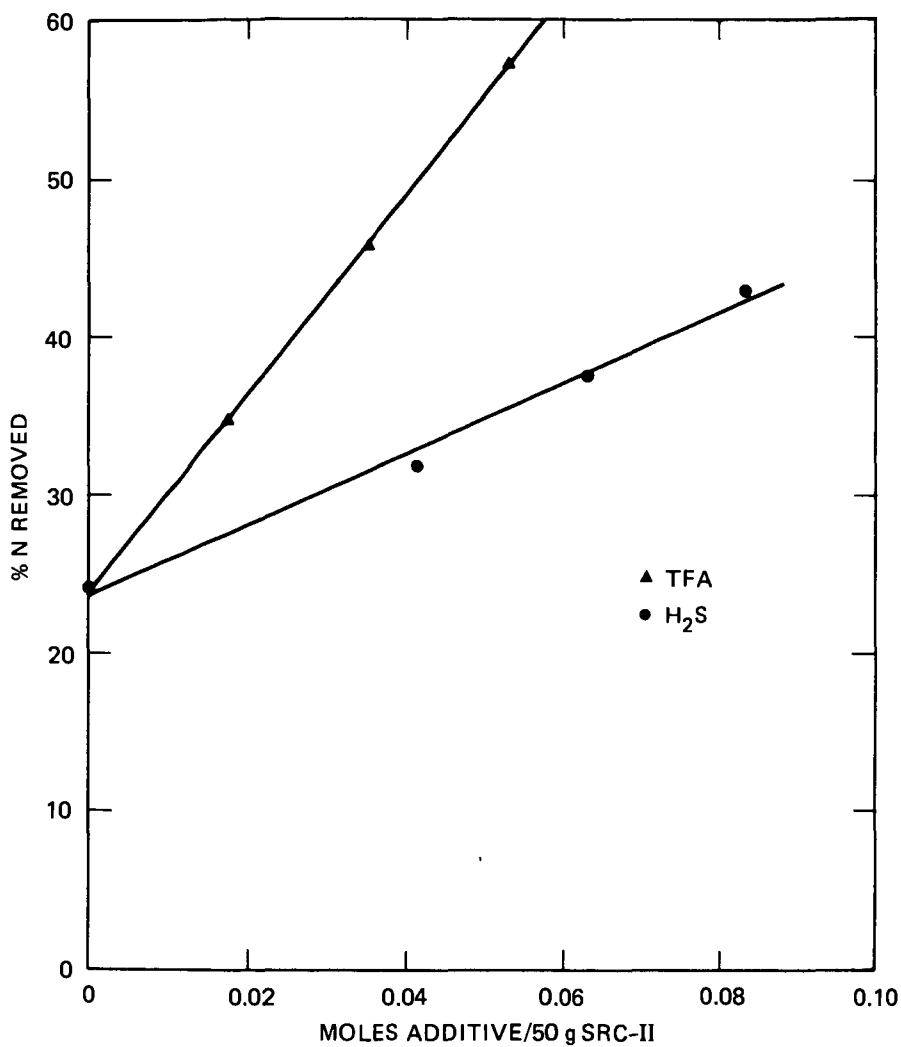
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FIGURE 1

EFFECT OF ADDITIVE ON HDN\*



\*1 h reaction of SRC-II liquid at 400°C with 1% sulfided CoMo catalyst and 1200 psig H<sub>2</sub>

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